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Cobalt(II) complexes of calix[6]arenes: Crystallographic studies into heteroatom bridge influence over discrete versus polymeric structure formation†**

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Supporting information:
CCDC 891014 and 891015 contains the supplementary crystallographic data for 1 and 2 respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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Calixarenes; Coordination Polymer; Complex

Abstract

Methylene-bridged calix[4]arenes have emerged as excellent ligands for polynuclear cluster formation. In this contribution methylene- and oxa-bridged calix[6]arenes have been examined as candidates for cluster formation with cobalt(II) nitrate, affording two markedly different structures. The nature of the structures is highly dependent on the bridging atoms. Reaction of *p*-tert-butylcalix[6]arene with cobalt(II) nitrate in DMF results in formation of a coordination polymer in which the calixarene adopts a 'double-partial' cone conformation. A similar reaction with *p*-tert-butyltetrahomodioxacalix[6]arene affords a discrete complex in which a central heteroatom also coordinates to the metal centre, with the calixarene in a 'double-cone' conformation. The synthesis and structure of both compounds is presented.

1. Introduction

Methylene-bridged calix[4]arenes (C[4]s) that adopt bowl conformations have emerged as versatile platforms for the construction of polynuclear metal cluster compounds [1-7]. Lower-rim deprotonation allows for the binding of transition or lanthanide metal centres (TM and LnM respectively), with the former bound preferentially over the latter when both are present. In recent studies we have shown that this approach can be used in the construction of a number of polynuclear clusters including $Mn(III)_2Mn(II)_2C[4]_2$ SMMs [2,3], enneanuclear $Cu(II)_9C[4]_3$ clusters that display versatile anion inclusion properties [4], $Mn(III)_4LnM(III)_4C[4]_4$ SMMs and magnetic refrigerants (depending on the LnM employed) [5,6] and $LnM(III)_6C[4]_4$ octahedra [7]. The coordination chemistry of the thia-, sulfonyl- and sulfinylcalix[4]arenes has received significant attention [8-11], but these supports display markedly different metal binding properties due to the presence of additional donor atoms in the ligand framework.

Given the aforementioned use of both methylene- and thia-bridged calix[4]arenes, we turned our attention to large calixarenes and oxacalixarenes as both represented comparatively underexploited sets of ligands for potential calixarene-supported cluster formation [for example see 12-20]. For the former this fact may be due to the inherent flexibility associated with the large calix[*n*]arene framework. We have recently shown that binuclear lanthanide C[8] complexes, that in fact exploit this feature, can be used as building blocks in the construction of larger polynuclear clusters based on a polyhedral expansion process [21]. Oxacalixarenes can be synthesised in various sizes, and via synthesis of particular oligomeric precursors, it is possible to introduce a desired number of ethereal bridges to the calixarene framework [22]. One particular benefit of using oxacalixarenes is that they allow one to tune ligand conformation (by introducing a specific degree of flexibility) and thus controllably vary the nature of metal binding by the resulting polyphenolic pocket [23-24]. *p*-tert-Butylcalix[6]arene (TBC[6]) and *p*-tert-butyltetrahomo-dioxacalix[6]arene (TBDOC[6]) are both readily accessible ligands (figure 1) that represent a step up in size from the general C[4] framework. The introduction of two ethereal bridges to the TBC[6] framework was thus a logical place to begin investigations

into controlled heteroatom inclusion for comparison with TBC[6]; TBDOC[6] is readily accessible via a trimeric precursor. Here we show that introduction of these ethereal bridges has a marked influence over the nature of Co(II) complexes formed in each case.

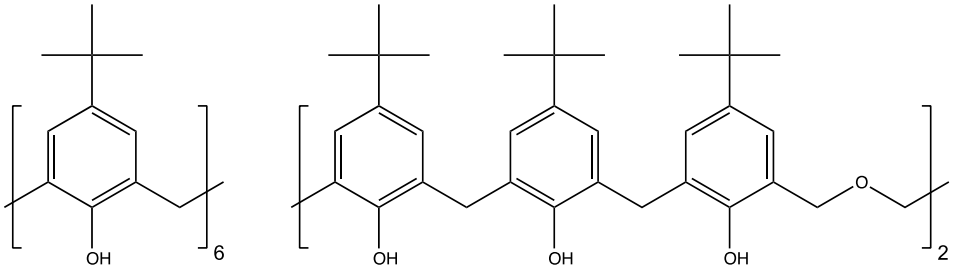

Figure 1. Schematic of TBC[6] and TBDOC[6], emphasising the presence of two ethereal bridges in the calixarene framework of the latter.

2. Experimental

2.1 Materials and Methods

TBC[6] [25] and TBDOC[6] [26] were synthesised according to literature procedures. All other chemicals were purchased from Aldrich and used as supplied.

2.2 Syntheses of complexes 1 and 2

A number of cluster forming reactions were explored using TBC[6] and TBDOC[6] in the presence of either cobalt(II) chloride hexahydrate or cobalt(II) nitrate hexahydrate. Single crystals formed in only two cases upon standing or slow evaporation and this occurred from a reaction involving cobalt(II) chloride for TBC[6] and cobalt(II) nitrate for TBDOC[6]. Crystals of **1** and **2** were readily obtained over a wide range of metal salt:calixarene stoichiometries.

Synthesis of $[Co^{II}(TBC[6]\text{-}2H)(dmf)_3]\cdot(dmf)_3$, 1: TBC[6] (100 mg, 0.103 mmol) and cobalt(II) chloride hexahydrate (125 mg, 0.526 mmol) were suspended in a mixture of methanol (7 ml) and DMF (7 ml) and stirred for 10 minutes. Sodium hydroxide (20 mg, 0.507 mmol) was added and the solution stirred for a further hour. Violet single crystals of **1** (42 mg, 28%) formed upon prolonged standing over a number of weeks. Anal. Calcd for $C_{84}H_{124}CoN_6O_{12}$ (%): C, 68.69; H, 8.51; N, 5.12. Found (%): C, 68.91; H, 8.52; N, 5.17. IR (cm^{-1}):

2954 (m), 2864 (w), 1672 (s), 1648 (s), 1481 (m), 1436 (w), 1375 (m), 1304 (w), 1253 (m), 1202 (m), 1090 (w), 869 (w), 819 (w), 683 (m).

Synthesis of [Co^{II}(TBDOC[6]-2H)(dmf)$_3$(H_2O)]·(dmf)$_{2.5}$(H_2O), 2: TBDOC[6] (100 mg, 0.097 mmol) and cobalt(II) nitrate hexahydrate (56 mg, 0.194 mmol) were suspended in a mixture of methanol (7 ml) and DMF (7 ml) and stirred for 10 minutes. Sodium methoxide (42 mg, 0.78 mmol) was added and the solution stirred for a further hour. Pale brown single crystals of **2** (48 mg, 34%) formed upon prolonged standing over several days. Anal. Calcd for $C_{81.5}H_{121.5}CoN_{4.5}O_{14.5}$ (%): C, 67.26; H, 8.42; N, 4.33. Found (%): C, 66.96; H, 8.36; N, 4.39. IR (cm^{-1}): 3409 (w), 2950 (m), 2864 (w), 1668 (s), 1653 (s), 1482 (s), 1456 (m), 1385 (m), 1302 (w), 1255 (w), 1213 (w), 1072 (w), 1019 (w), 873 (m), 796 (w), 680 (w).

2.3 X-ray crystallography

Data for **1** and **2** were collected on a Bruker X8 Apex II CCD Diffractometer operating with MoKα radiation (λ = 0.71073 Å) at 100(2)K.

***Crystal Data for 1 (CCDC 891014)*:** $C_{84}H_{124}CoN_6O_{12}$, *M* = 1468.82, Purple Block, 0.35 × 0.30 × 0.20 mm^3, monoclinic, space group $P2_1/n$ (No. 14), *a* = 18.8635(11), *b* = 18.6835(11), *c* = 24.5174(14) Å, β = 97.669(3)°, *V* = 8563.5(9) $Å^3$, *Z* = 4, $2\theta_{max}$ = 55.2º, 130649 reflections collected, 19675 unique (R_{int} = 0.0686). Final *GooF* = 1.014, *R1* = 0.0570, *wR2* = 0.1390, *R* indices based on 14324 reflections with I >2σ(I) (refinement on F^2).

***Crystal Data for 2 (CCDC 891015)*:** $C_{81.50}H_{121.50}CoN_{4.50}O_{14.50}$, *M* = 1455.26, Pale Brown Block, 0.40 × 0.30 × 0.25 mm^3, triclinic, space group *P*-1 (No. 2), *a* = 12.080(3), *b* = 14.865(3), *c* = 23.708(5) Å, α = 78.916(7), β = 86.496(7), γ = 84.827(7)°, *V* = 4156.6(16) $Å^3$, *Z* = 2, $2\theta_{max}$ = 53.7º, 62569 reflections collected, 17095 unique (R_{int} = 0.0725). Final *GooF* = 1.107, *R1* = 0.0759, *wR2* = 0.1822, *R* indices based on 9209 reflections with I >2σ(I) (refinement on F^2).

3. Results and Discussion

3.1 Description of Structures

3.1.1 Coordination polymer [Co^{II}(TBC[6]-2H)(dmf)$_3$]·(dmf)$_3$, 1.: Compound **1** results from reaction of TBC[6] with cobalt(II) chloride hexahydrate in a methanol / DMF solution in the presence of sodium hydroxide. The crystals are in a monoclinic cell and structure solution was carried out in the space group $P2_1/n$. The asymmetric unit (figure 2) comprises one TBC[6], one Co(II) centre (bound to a TBC[6] lower-rim O atom), three ligated DMF molecules and three DMF molecules of crystallisation. The most noticeable

feature of **1** is that the calixarene adopts the double-partial cone conformation in which three lower-rim O atoms are positioned on opposite sides of the TBC[6] annulus. Symmetry expansion around the Co(II) centre shows that the metal is five-coordinate and of trigonal bipyramidal geometry, with the fifth coordination site being in Figure 3A being filled by a symmetry equivalent lower-rim TBC[6] O atom. Similar analysis also shows that one ligated DMF molecule resides in a small cavity generated by the double-partial cone conformation in a symmetry equivalent TBC[6] molecule, forming two CH···π interactions with CH···aromatic centroid distances of 2.606 Å and 2.637 Å for one of the DMF methyl groups. The second methyl group of said DMF also forms two CH···π interactions with an aryl ring and has CH···aromatic centroid distances of 3.117 Å and 3.017 Å. Of the two remaining ligated DMF molecules, one lies between two back-to-back partial cone moieties from symmetry equivalent complexes and displays no significant interaction with either. The final ligated DMF is disordered over two positions and displays a weak interaction between a methyl group proton and the aromatic system of an adjacent symmetry equivalent molecule with a CH···aromatic centroid 3.318 Å.

Further symmetry expansion reveals formation of a 1-D coordination polymer wherein each partial cone assembles in a pseudo head-to-head fashion with a symmetry equivalent counterpart and results in large solvent regions in the structure. These are occupied by two crystallographically unique DMFs, one of which displays three CH···π interactions to TBC[6] aryl rings with CH···aromatic centroid interactions in the range of 2.548 Å - 2.821 Å. The coordination polymer chains themselves do not display any significant TBC[6]-TBC[6] interactions (figure 3B).

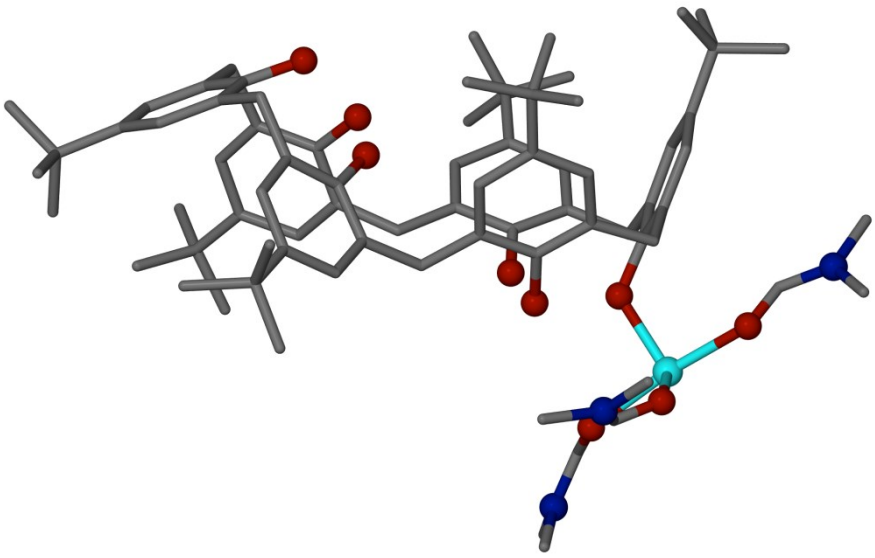

Figure 2. The asymmetric unit in **1** showing a) complexation of the trigonal bipyramidal Co(II) ion by the di-anionic TBC[6] (fifth coordination site of Co(II) being occupied by a symmetry equivalent lower-rim TBC[6] oxygen) and b) the double-cone conformation of TBC[6].

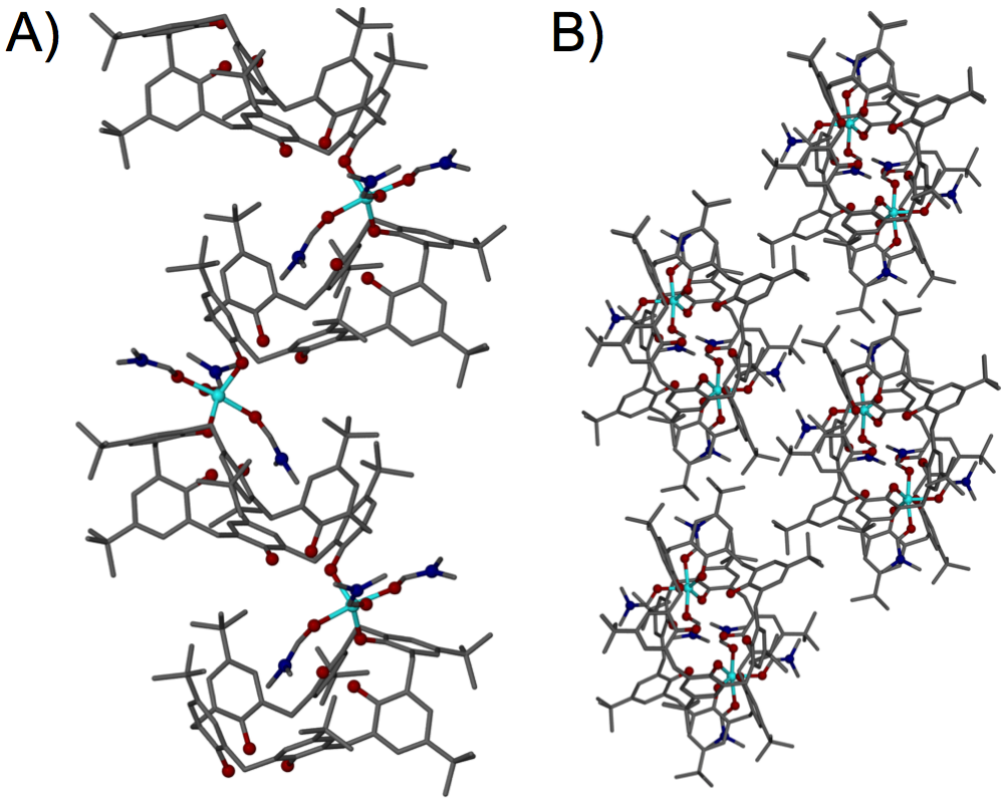

Figure 3. Extended structure of **1** showing the coordination polymer chain formed between TBC[6] and Co(II) ions. (a) The 1D chains form by linking through two TBC[6] lower-rim O atoms. (b) The chains pack together with no significant TBC[6]-TBC[6] interactions.

3.1.2 $[Co^{II}(TBDOC[6]\text{-}2H)(dmf)_3(H_2O)]\cdot(dmf)_{2.5}(H_2O)$, 2.: Compound **2** results from reaction of TBDOC[6] with cobalt(II) nitrate hexahydrate in a methanol / DMF solution in the presence of sodium methoxide. The crystals are in a triclinic cell and structure solution was carried out in the space group *P*-1. The asymmetric unit (figure 4) comprises one TBDOC[6], one octahedral Co(II) centre (bound to two TBDOC[6] lower-rim O atoms and one ethereal bridge), two ligated DMF molecules, one ligated water molecule and three DMF molecules of crystallisation. The most noticeable feature of **2** is that the calixarene adopts the double-cone conformation. In this conformation the ethereal oxygen atoms act like a flexible hinge that allows the ligand wrap around a metal atom in a fashion akin to the surface of a tennis ball, and results in the lower-rim hydroxyl groups pointing towards each other. The two ligated DMFs are exo to the calixarenes cavities and as such do not interact with the TBDOC[6] aromatic rings. The aquo ligand forms hydrogen bonding interactions with lower-rim hydroxyl groups (O···O distances 2.722 Å and 2.735 Å) as shown in figure 4. In addition there are four hydrogen bonds between the lower-rim hydroxyl groups that occur with OH···O distances in the range of 1.662 Å – 1.780 Å. Two of the three DMFs of crystallisation are disordered over two positions and were modeled at partial occupancies. One of these DMFs resides in one TBDOC[6]

cavity and forms several CH···π interactions with CH···aromatic centroid distances ranging from 2.519 Å - 2.874 Å.

Analysis of the extended structure of **2** reveals that numerous intermolecular interactions are present, and that discrete complexes interact in two directions. Expansion along one vector reveals that adjacent complexes of **2** assemble either in an edge-to-edge or an offset edge-to-edge fashion (figure 5a). In the former a ligated DMF ligand interacts with a long contact to an aromatic ring of its neighbouring complex (3.145 Å). In the latter case nearest neighbours are assembled such that a co-crystallised DMF lies in a pseudo cavity between two symmetry equivalent aromatic rings, albeit with the closest CH···aromatic centroid distance being 3.304 Å. Along the second direction symmetry equivalent complexes assemble in a linear chain as shown in Figure 5b. Further analysis reveals that a tert-butyl group of each discrete complex resides within the cavity of its symmetry equivalent nearest neighbour, forming a CH···π interaction with a CH···aromatic centroid distance of 2.924 Å.

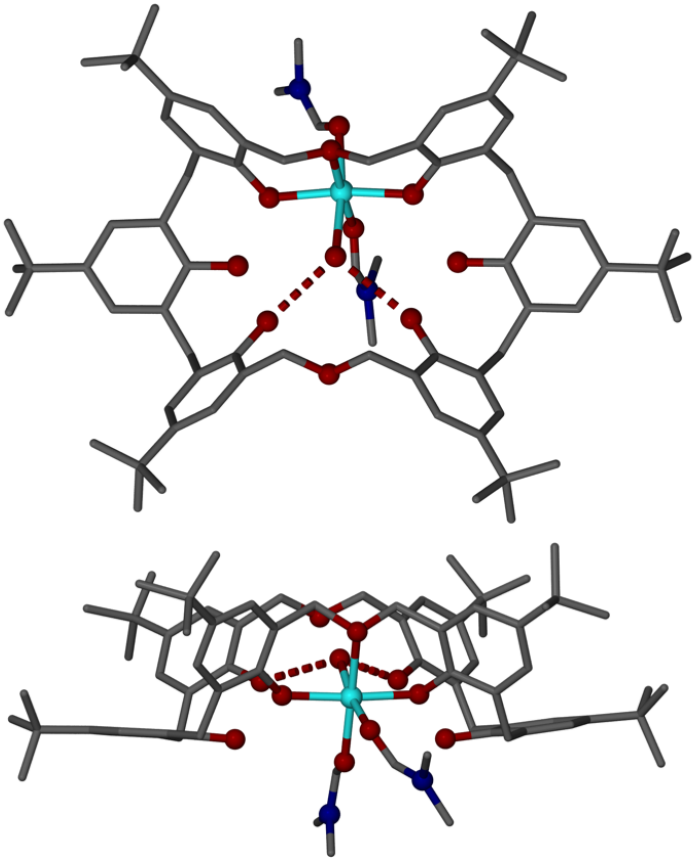

Figure 4. Two views of the asymmetric unit in **2** showing a) complexation of the octahedral Co(II) ion by the di-anionic TBDOC[6], b) coordination by the heteroatom bridge, c) hydrogen bonding interactions between the ligated aquo ligand and TBDOC[6] lower-rim OH groups (dashed lines) and d) the double-cone conformation of TBDOC[6].

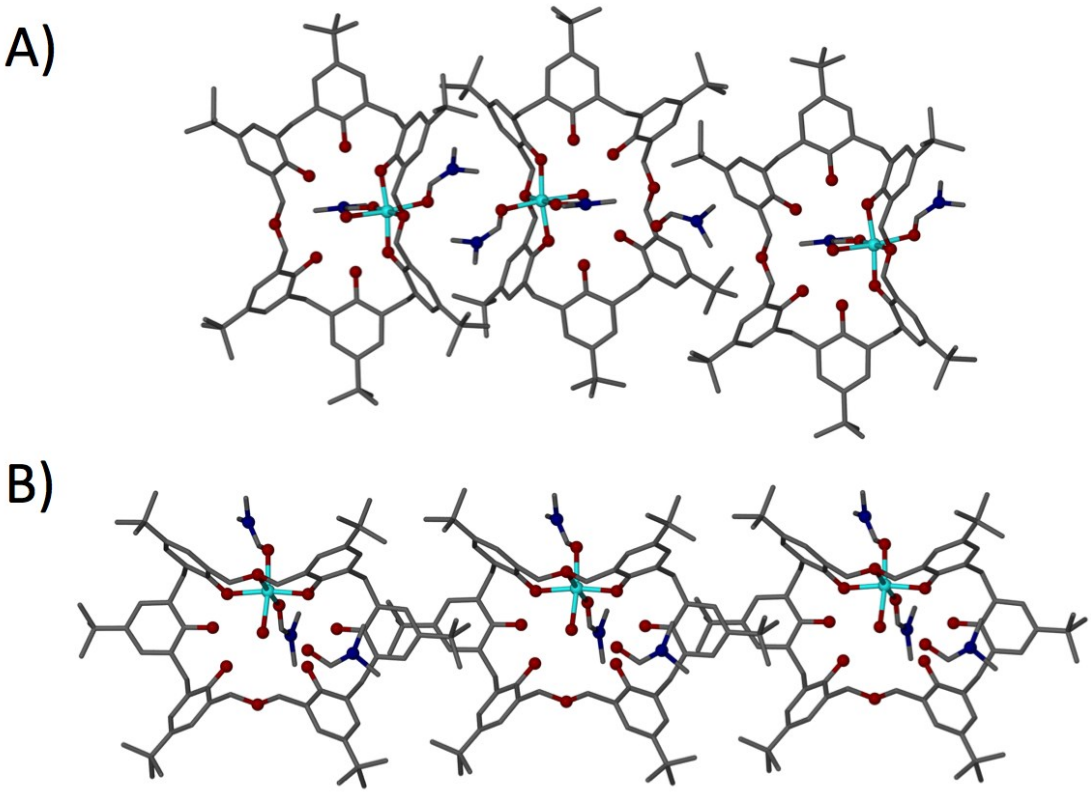

Figure 5. Extended structure of **2** showing the interaction of discrete complexes in two different directions. (a) Ligated DMF residing in cavity between symmetry equivalent complexes (b) Mutual inclusion of TBDOC[6] upper-rim tert-butyl groups in a cavity from a symmetry equivalent host in the double-cone conformation.

4. Conclusion

Calix[4]arenes are versatile supports for the formation of polynuclear TM and LnM clusters that have interesting magnetic properties [1-7]. Here we have begun to investigate the analogous chemistry of the hexameric analogues, but have not formed any polynuclear clusters to date. Although this is the case we have shown that TBC[6], when in the double-partial cone conformation, is capable of forming a 1-D coordination polymer with Co(II) centres. Introduction of two ethereal bridges to the general C[6] framework affords a more flexible platform that readily adopts the double-cone conformation upon complexation of a Co(II) centre. We are yet to form any large polynucelar clusters with methylene or oxa-bridged C[6]s, but results obtained with TBC[8] as a flexible cluster support suggest that this may well be possible through variation in the reaction conditions employed (e.g. base and metal ions utilised). If so, the resulting complexes may assemble in a polyhedral expansion process akin to that of TBC[8] [21].

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